DIRECT FREE ENERGY CALCULATIONS FOR GAS HYDRATES.

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Abstract.

In this work we present an efficient method for calculation of free energies for molecular crystals. This method is a generalization of the local harmonic approximation and allows full coordinate free energy minimization at finite temperatures and pressures. In terms of gas hydrates, this method provides a first principles route to the chemical potential of water in the hydrate lattice. This quantity has been calculated for different levels of cavity occupancy for the type I hydrate of methane. The values obtained indicate that the number of occupied cavities has a significant effect on the chemical potential of water. Further, we have used this method to calculate the total free energy of methane hydrate and ice. Using the integrated form of the equation of state for a Lennard-Jones fluid we have also calculated the free energy of the free guest species. With these three values the methane/ice/methane hydrate three-phase co-existence line can be obtained.

I. Introduction.

The ability to calculate free energy in an efficient manner is of paramount importance in the structural and thermodynamic study of gas hydrate systems. In principle, it is possible to fully characterize the structural and thermodynamic properties of the system from a knowledge of the free energy. In most cases, this involves calculating the structural or thermodynamic property as a function of temperature and pressure. If this is the case, the free energy must be calculated at many different state points. Thus the efficiency of the free energy calculation becomes the limiting factor and determines the scale of the calculations which can be undertaken.

The development of theories for free energy calculations on atomic solids based on local atomic vibrational behaviour has been an important contribution in this area[1]. In the Local Harmonic Model (LHM) the atoms are modelled as Einstein oscillators which vibrate in the field created by the other atoms, but there is no interatomic vibrational coupling. The LHM is computationally inexpensive and has been shown to give a good description of the thermodynamic properties of atomic solids[1]. It should be mentioned that analogous theories exist, notably the second moment model of Sutton[2], which is equivalent to the LHM only the nature of the approximation to the density of states differs. In this work we have further developed the LHM for complex molecular crystals and applied the theory to gas hydrates.

At present most attempts to explain the stability and properties of gas hydrates are based on the van der Waals and Platteeuw cell theory. According to this model the water molecules form a wee-defined crystal lattice containing cavities into which the guest molecules may be absorbed. The theory also assumes that the free energy of the water lattice is independent of which molecules, if any, occupy the cavities. Thus the contribution of the water lattice to the total free energy of the system must be the same when all the cavities are empty as when all the cavities are occupied. Recent computer simulations by Rodger[3] indicate some fundamental difficulties with the van der Waals and Platteeuw theory. His results indicate that the empty lattice is unstable rather than metastable. If this is the case, the guests must serve to dampen out the critical lattice vibrations that lead to the rearrangement of the host lattice. Tanaka[4] has considered distortion of hydrate cages around xenon and carbon tetrafluoride guests. The work showed that the smaller xenon atoms did not distort the hydrate cages, while the carbon tetrafluoride caused significant distortion of the small cages. This deformation gave rise to a change in the water chemical potential and casts further doubt on the validity of the primary assumption of the cell theory.

In this paper we present the extension to the LHM for molecular crystals and its application to gas hydrates. The method provides a simple, computationally cheap tool for the investigation of the lattice relaxation in gas hydrates and their structural and thermodynamic properties. We present optimum cell lengths over a range of temperatures and pressures for methane hydrate obtained using a single co-ordinate free energy minimisation and a range of other properties. Also we present values of the free energy difference between ice and the β-hydrate, and between the β-hydrate and the water lattice of hydrates of various occupancies. We demonstrate how the three phase line (ice-hydrate-vapour) can be calculated using this method. Finally, we show the necessity for a full co-ordinate (i.e. all atomic co-ordinates) free energy minimisation rather than the single co-ordinate (i.e. unit cell length) calculation using the dissociation pressure calculated using each method compared to the experimental value.

Method.

The essence of the LHM is the ease of calculation of the vibrational partition function, q_{vib}

$$q_{vib} = \frac{1}{1 - e^{-\frac{h\upsilon}{k_B T}}} \tag{1}$$

which is simple to calculate from the vibrational frequency, υ

$$\upsilon^2 = \frac{\partial^2 U}{\partial r^2} \frac{1}{4\pi m^2} \tag{2}$$

The Helmholtz free energy can then be calculated from

$$A = -k_B T \ln q_{vib} \tag{3}$$

In the classical limit, where $k_B T$ is much greater than $h\upsilon$, equation (1) simplifies to

$$q_{vib} = \frac{k_B T}{h\upsilon} \tag{4}$$

For a perfect crystal with a unit cell of N atoms, the quasi-harmonic approximation gives the Helmholtz free energy as

$$A = U + kT \sum_i^{3N} \ln\left(2 \sinh\left(\frac{h\upsilon_i}{2kT}\right)\right) \tag{5}$$

where U is the potential energy and the vibrational frequency of atom i, υ_i, is obtained from the dynamical matrix with elements

$$D_{ij} = \frac{\partial^2 U}{\partial r_i \partial r_j} \tag{6}$$

as the square root of the eigenvalues of the matrix $M^{-1}D$, where M is the mass matrix. In the LHM, D_{ij} is set to zero unless i and j refer to co-ordinates of the same atom. Thus D is reduced from a $3N \times 3N$ matrix to N 3×3 matrices and the diagonalisation becomes substantially easier. Equation (5) is, therefore, a 3-dimensional, many-atom representation of equation (3).

However, for a molecular system, this neglect of interatomic coupling is only valid for atoms in different molecules. Within the same molecule the vibrations of the atoms are strongly coupled through the presence of covalent bonds. So, in the Molecular Local Harmonic Model (MLHM), the dynamical matrix can still be reduced to block diagonal form, except in this case each block represents a set of molecular co-ordinates rather than a set of atomic co-ordinates. Thus D is reduced to M 9×9 matrices. The expression for the Helmholtz free energy in the MLHM is

$$A = U + kT \sum_i^m \sum_j^{N_i} \ln\left(2 \sinh\left(\frac{\hbar\omega_{j,i}}{2kT}\right)\right) \tag{6}$$

where N_i is the number of atoms in molecule i, m is the number of molecules and $(\omega_{ij})^2$ are the eigenvalues of the molecular matrices $M_i^{-1}D_i$.

We have used the SPC model[5] for water and a single Lennard-Jones site for the methane. Using a grid search method we have performed a single co-ordinate minimisation by calculating the free energy over a range of unit cell lengths. This is a simple application of the MLHM and provides optimum cell lengths and gradient properties such as thermal expansivity, isobaric compressibility and heat capacities. We have also performed full atomic co-ordinate free energy minimisation using a conjugate gradient-type approach, where the atoms are moved according to the free energy force. For the calculation of hydrate dissociation pressures we have used an equation of state for a Lennard-Jones fluid[6] to describe the properties of the fluid guest.

III. Results.

In figure 1(a) we show the effect of temperature on the unit cell length of methane hydrate at 1 atmosphere. It is noticeable that the effect is linear and that the cell length values obtained are comparable with those of experiments[7]. In figure 1(b), we show the effect of pressure on the unit cell length of methane hydrate at 260 K. Again, the effect is linear and the cell length values are similar to experimental values[8]. The thermal expansivity calculated using the values shown in figure 1(a) is 1.78×10^{-4} K^{-1}. This compares favourably with 0.77×10^{-4} K^{-1} obtained experimentally by Tse et al.[9]. The compressibility calculated from figure 1(b) is 3.3×10^{-11} Pa^{-1}, which compares well with the estimate of 14×10^{-11} Pa^{-1} given by Sloan[10]. The heat capacities calculated from our work are of the order of 50 to 55 J mol^{-1} K^{-1}, which is are a factor of 4 to 5 smaller than the experimental values of Handa[11].

Initial observations of these results suggest that there is some effect of the guest molecules on the host lattice. The difference in Gibbs free energy between the β-hydrate and the water lattice of the occupied hydrates is approximately 1.1 kJ/mol. These differences are very similar to empirical estimates obtained by the cell theory for the free energy difference between the hydrate water lattice and ice (1.2-1.3 kJ/mol at 273 K[12]). There are also differences between the Gibbs free energies of the water lattices of the occupied systems. This difference is approximately 0.1 kJ/mol. On closer inspection, inclusion of guest molecules appears to stabilise the water lattice. However, it seems that enhanced stability and guest inclusion have a complex relationship. The fully occupied methane hydrate may have the lowest total Gibbs free energy, but it does not have the most stable water lattice. Occupation of the two 5^{12} cavities has the greatest stabilising effect on the water lattice.

There seems to be some degree of variation of the effect of guest molecules on the host water lattice with temperature and pressure. The biggest differences, around 1.1 kJ/mol, are experienced at the higher temperatures and lower pressures that we have studied. These are precisely the conditions of interest in industrial applications. Given that the magnitude of these changes in the free energy of the water lattice, ΔG_{H}, is comparable with $\Delta\mu_w^{\beta}$, it must be expected that the accuracy of the cell theory predictions will vary with composition. At low temperatures and higher pressures the difference is considerably smaller, about 0.2 kJ/mol.

From the full atomic co-ordinate free energy minimisation we observe similar trends, such that the fully occupied hydrate is always the most stable hydrate, but the hydrates of intermediate occupancy have the more stable water lattice than either the β-hydrate or the fully occupied hydrate. The magnitude of ΔG_{H} seems to be temperature dependent, so that at higher temperatures the difference is larger. This is a reflection of the fact that the free energy minimisation is entropy driven. Our calculations show that ΔG_{H} can be as high as 2.3 kJ/mol at higher temperatures. Such differences in the thermodynamic properties are currently ignored in the cell theory, which assumes that the properties of the water lattice of occupied hydrates are the same as the β-hydrate. Thus $\Delta\mu^{\alpha-\beta}$ in the cell theory ignores any occupancy-dependent properties. Holder and Hand[13], for example, used an optimum value for $\Delta\mu^{\alpha-\beta}$ of 1.115 kJ/mol. It is clear that occupancy-dependent changes in $\Delta\mu^{\alpha-\beta}$ of about 2.3 kJ/mol will be very significant and inclusion of such guest perturbation of the host lattice will be necessary to correct errors experienced when using the cell theory to determine hydrate dissociation pressures.

The MLHM, when coupled with an appropriate equation of state to describe the thermodynamics of the bulk guest phase, can be used to calculate hydrate dissociation pressures by calculating points on the ice/gas/hydrate phase line. We have used results from the unit cell optimisation and the full co-ordinate minimisation in order that we may determine whether the full co-ordinate minimisation is necessary to correctly describe gas hydrate properties, or whether the single co-ordinate minimisation is sufficient. In figure 2, we illustrate the dissociation pressure calculated using the unit cell optimisation. The point where the two lines cross indicates the dissociation pressure and in this case, methane hydrate at 270 K, it is approximately 40 MPa. In figure 3, we illustrate the case for full co-ordinate minimisation. Here we calculate the dissociation pressure to be 2.5 MPa. This is in excellent agreement with the experimental value[8] of 2.32 MPa. The quality of this agreement must be contemplated given the errors within the SPC model[14], although SPC water has been shown to yield the correct melting temperatures for methane hydrate[15].

IV. Conclusions.
In this paper we have shown the development of a simple model for free energy minimisation of complex molecular crystals. We have applied this model to gas hydrates and shown that calculation of thermodynamic properties using this method yields values in good comparison to experiment. We have demonstrated the importance of lattice relaxation in the calculation

of some of these properties and illustrated this using the calculation of dissociation pressure as an example.

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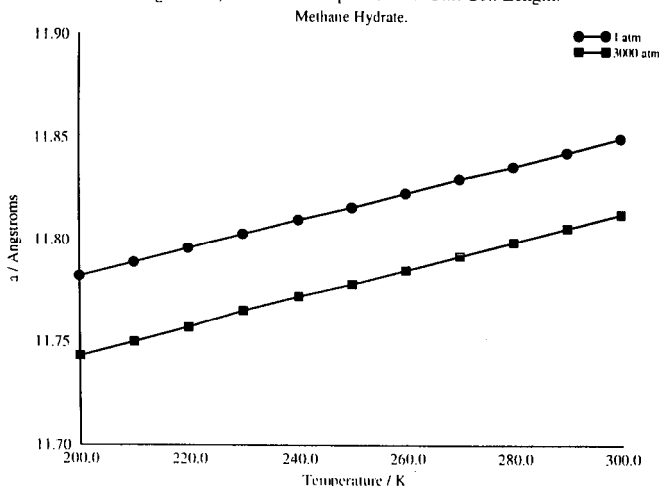
Figure 1(a) Effect of Temperature on Unit Cell Length.
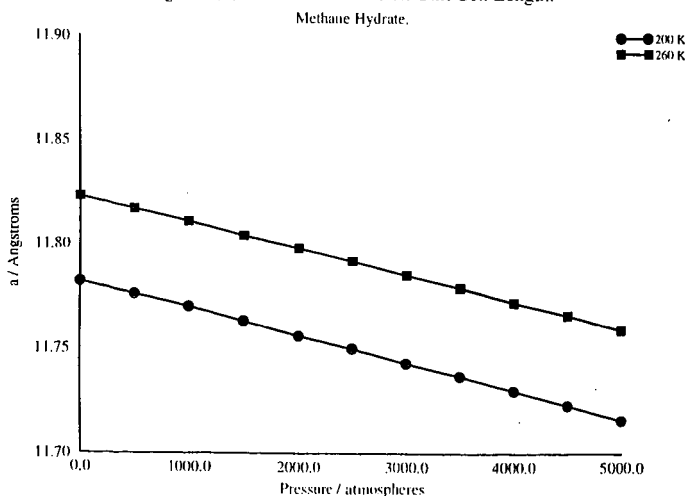

Figure 1(b) Effect of Pressure on Unit Cell Length.

Figure 2. Dissociation Pressure of Methane Hydrate.
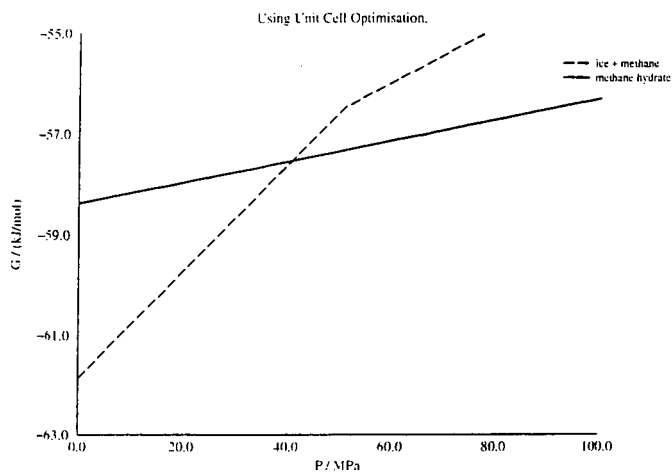

Using Unit Cell Optimisation.

Figure 3. Dissociation Pressure of Methane Hydrate.
Using full coordinate optimisation.